

Molecular Transformations in the Processing Sequence
Pyrolysis-Hydrotreating with Utah Oil Sands

by

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INTRODUCTION

The utilization of Utah's Uinta Basin oil sands resource will most likely involve a combination of in-situ and mining-surface recovery techniques. It has been reported that 15-30% of Utah's oil sands are amenable to mining-surface recovery processes.⁽¹⁾ The mining-surface recovery processes include aqueous separation,⁽²⁻⁴⁾ solvent extraction^(5,6) and pyrolysis.⁽⁷⁻¹⁹⁾ The production of refinery feedstocks from mined oil sands can be accomplished by a number of processing sequences: aqueous separation or solvent extraction followed by coking or hydrotreating of the full range bitumen and rotary kiln or fluidized bed pyrolysis followed by hydrotreating of the bitumen-derived liquid.

The objective of this investigation was to explore the molecular transformations that occurred in the processing sequence pyrolysis of the mined oil sand ore in a fluidized bed⁽¹⁵⁾ followed by hydrotreating of the bitumen-derived liquid⁽²⁰⁾.

EXPERIMENTAL METHODS AND MEANS

Fluidized Bed Pyrolysis System

The bitumen-derived liquid used in the hydrotreating studies was produced from the Whiterocks tar sand ore in a large diameter fluidized bed pyrolysis reactor. The reactor temperature ranged from 773 to 813 K, and the average feed sand retention time was 17.2 minutes during the course of the production run.

The production of the bitumen-derived hydrocarbon liquid from the Whiterocks tar sand has been described in detail by Sung⁽¹⁵⁾.

Hydrotreater Process Unit

Process studies were conducted in a fixed bed reactor which operated in an upflow mode to minimize thermal gradients in the catalyst bed and to ensure complete wetting of the catalyst. A schematic of the hydrotreater system is presented in Figure 1. The reactor was designed for operation at a maximum pressure of 34.5 MPa at 773 K. The catalyst was diluted with quartz sand (50% by volume) in the inlet region of the bed (~20%) to trim the exotherm caused by olefin hydrogenation reactions.

The base case operating conditions for the hydrotreating study were as follows: reaction temperature, 619 K (653 °F); liquid hourly space velocity (LHSV), 0.5 h⁻¹; total reactor-pressure, 13.7 MPa (1980 psia) and hydrogen-to-hydrocarbon feed ratio, 890 m³/m³ (5000 scf/bbl). The API gravity of the total liquid product was constant at 23.2 °API after the reactor was on-stream for 94 hours at the base case conditions. At this point, it was assumed that the catalyst had attained a stationary state and that 95% of the coke deposition had occurred. A series of experiments were conducted in which the system was operated in a cyclic mode (base case condition/desired reaction condition/base case condition) for approximately 1000 hours. The total liquid product from each experiment was collected for analyses. The analytical test procedures conformed to those outlined in the ASTM manuals.

Mass balances were taken for 3 hours at the end of a 16-hour line-out period after the system had attained a stationary state at the new reaction conditions. The mass balances were conducted by monitoring the liquid fed to the reactor system for discrete time periods. At the conclusion of each mass

balance the collected gas and liquid samples were weighed and the gas sample was weathered into a vapor collector and analyzed by gas chromatography. All the mass balances were greater than 97.5 wt%.

The extent of nitrogen removal was the key reactivity parameter followed during the course of the study; however, the key operating parameter followed on the catalyst testing unit during the run was the specific and/or API gravity of the total liquid product.

Catalyst

A UNOCAL quadralobe Ni/Mo/Al₂O₃ hydrodenitrogenation (HDN) catalyst was used in this study. The catalyst contained 3.3 wt.% NiO, 12.8 wt.% MoO₃, and 0.8 wt.% P₂O₅. It had a surface area of 241 M²/g and a pore volume (Hg porosimetry) of 0.55 cm³/g. The sulfiding conditions were specified by the catalyst manufacturer. A solution of dimethyl disulfide in kerosene (~ 2 wt% sulfur) was used to sulfide the catalyst at a LHSV of 1.0 h⁻¹. The hydrogen-to-sulfiding solution ratio was 890 m³/m³ (5000 scf/bbl). The reactor temperature was adjusted to the initial run temperature after sulfur breakthrough at which point the sulfiding solution was discontinued.

A description of the experimental apparatus and operating procedures; a description of the catalyst and the catalyst activation procedures; and a summary of the process variable study have been reported by Longstaff, et al²¹. The design, construction and operation of the hydrotreater catalyst testing unit have been discussed in detail by Longstaff²⁰.

Analysis of Liquid Products

Simulated Distillation The boiling point distributions of the hydrotreated products were determined by simulated distillation. The samples were dissolved in dichloromethane and the analyses were performed on a programmed Hewlett-

Packard Model 5730 A gas chromatograph: the oven temperature was programmed from 243 to 623 K at 11°C/minute and was held at 623 K for 16 minutes; the injector temperature was initially set at 523 K and raised to 633 K after 12 minutes and the FID detector temperature was 673 K. The boiling point temperatures were calibrated with a standard mixture of normal paraffins (C_5 - C_{44}).

Gas Chromatography-Mass Spectrometry Analysis The bitumen-derived liquid feed and the hydrotreated total liquid products were analyzed with a gas chromatograph (Hewlett-Packard Model 5890 A) using a fused silica capillary column coated with 5% phenyl methyl silicone bonded stationary phase (30m x 0.25mm ID, DB-5, J & W scientific). The temperature program was ranged from 323 K to 573 K at 3°C min⁻¹, with a hold at 573 K for 20 minutes.

Gas chromatography - mass spectrometry analyses were performed on a Finnigan MAT95 high resolution gas chromatograph/mass spectrometer (Finnigan MAT ICIS II operating system) fitted with a DB-5 gas chromatographic column (30m x 0.25mm ID).

RESULTS AND DISCUSSION

The bitumen-derived liquid was significantly upgraded relative to the native bitumen (Table 1): 19.1 °API versus 11.9 °API; a viscosity of 85.4 cps @ 289 K, versus 2665 cps @ 358 K; a volatility (<811 K) of 82.2 wt.% versus 40.5 wt.%; a Conradson carbon residue of 4.7 wt% versus 8.1 wt%; etc., respectively. The atomic hydrogen-to-carbon (H/C) ratio of the bitumen-derived liquid was lower than that of the native bitumen. This reduction was related to dealkylation reactions during pyrolysis which resulted in the production of a more aromatic hydrocarbon liquid and consequently a lower H/C ratio. Furthermore, the asphaltene fraction in the native bitumen was assumed to be the primary precursor of the carbonaceous residue deposited on the spent sand thus the coking tendency

of the bitumen-derived liquid during hydrotreating was expected to be less than that of the native bitumen.

Identification of individual compounds in the volatile fractions (811 K) of the Whiterocks bitumen, the bitumen-derived liquid and the hydrotreated total liquid was based on the comparison to known spectra from the literature or were tentatively assigned based on interpretation of the mass spectrum.²²⁻³⁴ Major compound types found in the 1000°F minus fraction of the native Whiterocks bitumen were substituted and unsubstituted cyclohexanes, benzenes, decalins, tetralins, naphthalenes perhydrophenanthrenes (tricyclic terpanes), octahydrophenanthrenes, tetrahydrophenanthrenes, phenanthrenes, phenyl (cyclohexyl) alkanes, indan (cyclohexyl) alkanes, perhydrochrysenes (17,21-secohopanes), steranes (C_{27} - C_{29}), hopanes (C_{27} - C_{35}) and traces of paraffins. Heterocyclics such as benzofuran, indoles, quinolines, carbazoles and tricyclic and pentacyclic carboxylic acids were also detected.

Basically, the compounds types identified in the Whiterocks bitumen-derived liquid were similar to those identified in the volatile fraction of the bitumen. Several additional compound types were also identified: normal alkanes (C_7 - C_{30}) and α -alkenes, branched alkanes (C_7 - C_{28}) and alkenes, cyclopentanes, styrenes, indenenes, dihydronaphthalenes, dihydrophenanthrenes, and the olefin related to perhydro- β -carotane. The amounts of alkylnaphthalenes and alkylphenanthrenes increased in the bitumen-derived liquid compared with the bitumen. The hydrotreated bitumen-derived liquid consisted primarily of saturated compounds, such as alkanes (normal and branched) and cycloalkanes (1-5 rings). It also contained low concentrations of aromatic compounds which were predominantly monoaromatics.

The task of identifying the thermal reactions pathways in bitumen pyrolysis

was difficult due to the complexity of the native bitumen. However, several pathways were rationalized through the structural identifications of these three samples. These reactions included cleavage of long side chain, dehydrogenation, polymerization and condensation, and decarboxylation.

The normal and branched (mostly isoprenoid) alkanes and normal and branched-1-alkenes generated in the pyrolysis reactions probably originated as alkyl groups attached to aromatic rings in multi-ringed aromatics and naphenoaromatics and/or from alkyl bridges between two aromatic clusters, two naphthenic clusters, and/or an ermoatic cluster and a naphenoaromatic cluster. Since these types of compounds were not found in the 811 K minus fraction of the bitumen, it was presumed that they were present in the high boiling, residual fraction of the bitumen.

The speculation regarding the pyrolysis reaction pathways was confirmed by gradient elution chromatography⁽³⁵⁻³⁷⁾ analysis of the native bitumen and the bitumen-derived liquids produced during the rotary kiln pyrolysis⁽¹⁸⁾ of the Whiterocks tar sand (Table 2). The breaking of alkyl linkages between clusters followed by dealkylation led to a reduction in the asphaltene content of the bitumen-derived liquid and to a large increase in the mono-, and dinuclear aromatic contents of these liquids.

The presence of alkyl indenenes, dihydronapthalenes, dihydrophenathrenes and the increased amounts of the alkyl naphthenes and phenanthrenes suggested that step-wise dehydrogenation of hydroaromatics occurred. The hydroaromatics present in the bitumen could have acted as hydrogen donors during pyrolysis.

Hydrogen was produced during the pyrolysis of oil sand. The formation of hydrogen was believed to have occurred via a gas phase reaction, coincident with light oils production and a solid reaction, associated with the formation of the

carbonaceous residue on the sand grains.⁽³⁸⁾ The clays in the solid substrate may have been activated at pyrolysis conditions and may have catalyzed polymerization and condensation of aromatics and hydroaromatics during pyrolysis. These reactions would be expected to be accompanied by the formation of hydrogen.

Small amounts of carbon dioxide were detected in the produced gases during pyrolysis of the Whiterocks oil sand. It was presumed that the CO₂ was produced by thermal decomposition of carboxylic acid functional groups present in the native bitumen. The decomposition of the R-COOH bonds readily occurred at the pyrolysis temperatures (723-823 K).⁽³⁸⁾ It was presumed that the CO₂ concentration would have been higher if the source of CO₂ had been related to the decomposition of mineral carbonates which were present in the reservoir rock.

Hydrogenation, hydrogenolysis and heteroatom removal were the principal reactions which occurred in the hydrotreater. The absence of olefins in the hydrotreated products and the heat released in the inlet region of the catalyst bed, suggested that hydrogenation of olefinic bonds occurred readily during hydroprocessing. The predominance of hydroaromatic species in the total liquid product indicated that polycyclic aromatics underwent partial hydrogenation. The naphtha and middle distillate fractions were formed via thermal and catalytic reactions at hydrotreating conditions.

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| | Native Stirmon | Stirmon-Derived Lipids | Hydrated Stirmon-Derived Lipid |
|-------------------------------|-------------------|---------------------------|--------------------------------------|
| API density | 11.9 | 18.5 | 35 |
| Conc'dn. Coeff. Residue wt | 0.1 | 4.7 | NA |
| Poor Peptide E | 330 | 379 | 159 |
| Elemental Analysis | | | |
| Volatility, wt % | 60.5 | 62.2 | 62.6 |
| Wt % | 10.0 | 10.0 | 10.0 |
| 120 - 137 % wt | 0.0 | 6.7 | 12.5 |
| 137 - 161 % wt | 4.9 | 18.5 | 40 |
| 161 - 201 % wt | 33.6 | 39.0 | 34.0 |
| >201 % wt | 5.5 | 17.8 | 2.6 |
| Elemental Analysis | | | |
| C, wt % | 85.1 | 85.9 | 86.7 |
| H, wt % | 11.0 | 11.1 | 11.3 |
| N, wt %/ppm | 0.1 | 0.1 | 45 ppm |
| O, wt %/ppm | 0.6 | 0.6 | 16 ppm |
| W, wt % | 1.1 | 1.5 | 1.5 |
| Wt, ppm | 63 | 9 | NA |
| P, ppm | <1 | <1 | NA |

| Run ID | Device Stream | PR-102-1 | 102-102-2 | PR-102-3 | PR-102-4 |
|---|---------------|----------|-----------|----------|----------|
| Reaction | | | | | |
| Temperature, K | | 790 | 790 | 780 | 780 |
| Reactor | | | | | |
| Reactor Retention Time, min. | | 31 | 31 | 19 | 9 |
| ED Bed Flow Rate | | | | | |
| MCFO | | 77.5 | 77.5 | 77.1 | 77.4 |
| Gradient Elution Chemicals/Conc. | | | | | |
| Acetonitrile | | | | | |
| wt. % | 10.3 | 10.3 | 11.7 | 0.4 | 13.5 |
| Wt./Vol. wt. % | 9.3 | 23.7 | 41.7 | 40.4 | 39.7 |
| Wt. oil | 31.3 | 10.1 | 10.0 | 11.9 | 11.3 |
| Acidic resin | | | | | |
| wt. % | 17.0 | 12.4 | 12.9 | 13.0 | 12.3 |
| Basic resin | | | | | |
| wt. % | 9.0 | 0.0 | 1.3 | 1.1 | 1.9 |
| Polar resin | | | | | |
| wt. % | 1.4 | 1.3 | 1.7 | 1.7 | 1.3 |
| Aliphatic resin | | | | | |
| wt. % | 29.4 | 12.0 | 12.9 | 15.1 | 9.0 |
| Nonaromatic Aliphatic resin | | | | | |
| wt. % | 16.9 | 0.4 | 3.2 | 9.3 | 3.9 |